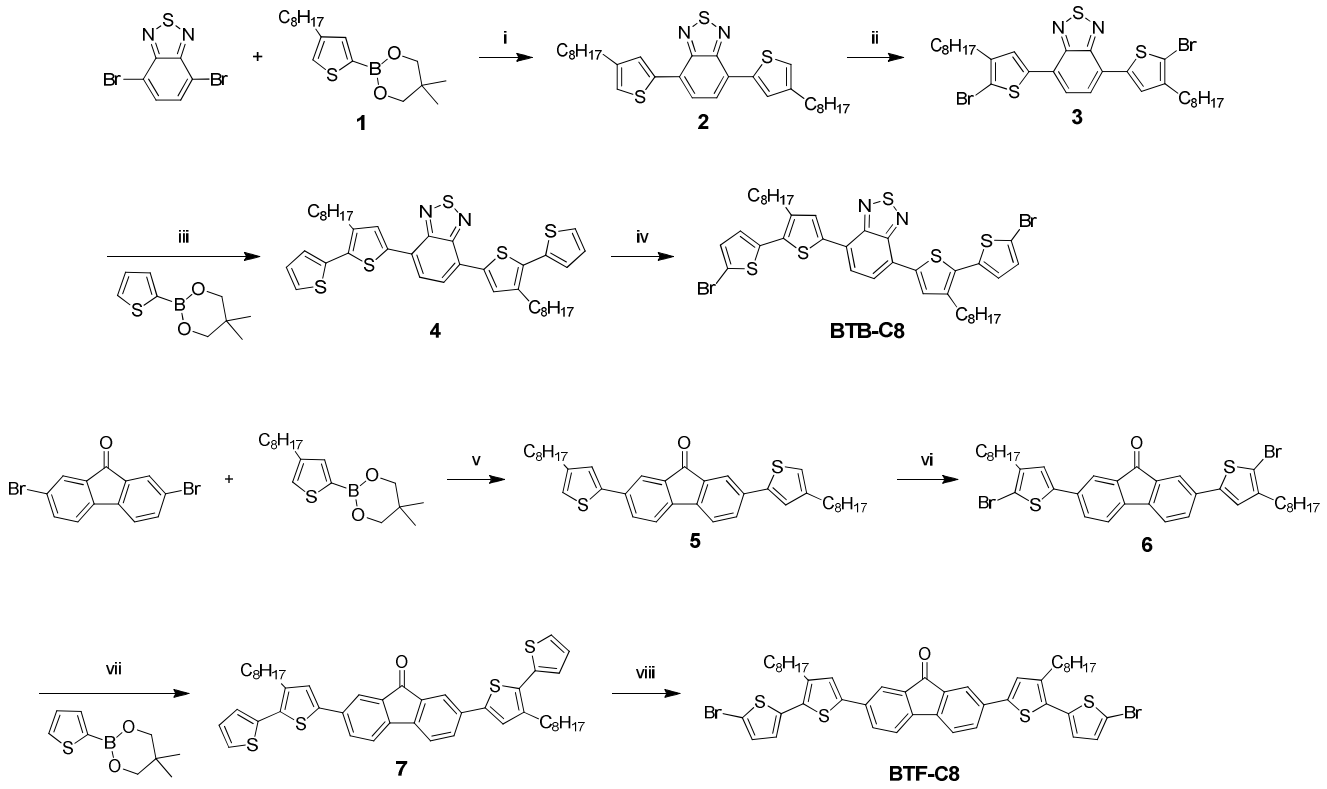
Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis, optoelectronic and photovoltaic properties of conjugated alternating copolymers incorporating 2,1,3-benzothiadiazole or fluorenone units: a comparative study

Nicolas Delbosc, Wan Zaireen Nisa Yahya, Noella Lemaitre , Solenn Berson,
Franz Fuchs, Benjamin Grévin, Jérôme Faure-Vincent, Jean-Pierre Travers and Renaud Demadrille*

Electronic Supporting Information

Table of contents:



Scheme S1 : Step by step synthesis of fluorenone (**BTF-C8**) and benzothiadiazole (**BTB-C8**) monomers with linear alkyl chains : (i) $Pd(Ph_3)_4$, THF, K_2CO_3 2M, reflux (ii) NBS, $CHCl_3$, RT (iii) $Pd(Ph_3)_4$, K_3PO_4, DMF, reflux (iv) NBS, $CHCl_3$, RT (v) $Pd(Ph_3)_4$, K_3PO_4, DMF reflux (vi) NBS, $CHCl_3$, RT (vii) $Pd(Ph_3)_4$, K_3PO_4, DMF, 100°C (viii) NBS, $CHCl_3$, RT.

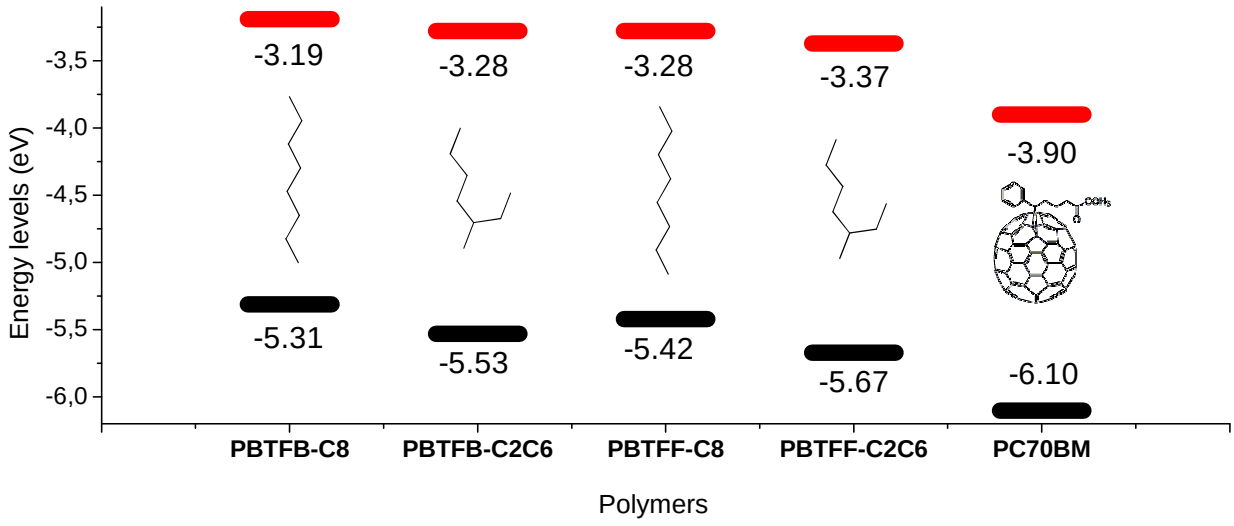


Figure S2: Graphical representation of orbital frontiers energy level of polymers and PC70BM.

Table S3: Photovoltaic parameters of polymers **PBTFB-C8** and **PBTFF-C8** blended with PC60BM or PC70BM incorporated in active layer of devices with architecture ITO/PEDOT:PSS/active layer/Ca/Al.

Polymer	Acceptor (ratio D:A)	Solvent processing	Voc (V)	Jsc (mA/cm²)	FF	η (%)
PBTFB-C8	PC60BM (1:1)	CB	0.84	2.78	0.28	0.65
	PC60BM (1:2)	CB	0.74	4.62	0.34	1.16
	PC70BM (1:1)	CB	0.85	3.44	0.28	0.81
	PC70BM (1:2)	CB	0.79	6.6	0.33	1.73
PBTFF-C8	PC60BM (1:1)	CB	0.86	2.65	0.29	0.66
	PC60BM (1:2)	CB	0.76	3.42	0.31	0.81
	PC70BM (1:1)	CB	0.76	3.93	0.30	0.90
	PC70BM (1:2)	CB	0.83	6.13	0.36	1.82

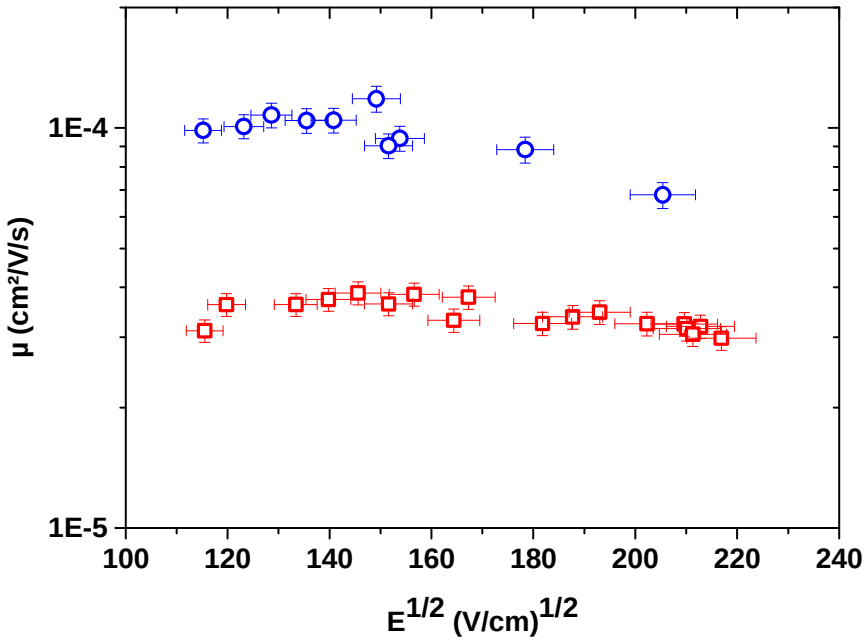


Figure S4: Evolution of the mobility vs. $E^{1/2}$ (E is the applied electric field) for the PBTFB-C2C6:[70]PCBM solar cells with 1:3 (open blue dots) and 1:4 (open red squares) ratios.

Experimental Section

Materials:

All reagents and chemicals were purchased from Aldrich, Acros or Kaironkem and used as received, except for THF which was distilled over sodium–benzophenone prior to use. Thin layer chromatography was performed on silica gel-coated aluminium plates with a particle size of 2–25 mm and a pore size of 60 A°. Merck 60 (70–230 mesh) silica was used for flash chromatography.

Characterisation techniques:

All synthesized monomers and polymers were characterized by ^{1}H and ^{13}C NMR and elemental analysis. NMR spectra were recorded on a Bruker AC 200 MHz spectrometer. Chloroform-d ($CDCl_3$) containing TMS as an internal standard, is used as solvent. Elemental analyses (C, H, N, and S) were carried out by CRMPO at the university of Rennes 1 (France).

UV-vis absorption spectra were recorded in chloroform solution and in thin film on a Perkin-Elmer Lambda 2 spectrometer (wavelength range: 300–900 nm; resolution: 2 nm). Molecular weights of the polymer fractions (obtained by Soxhlet extraction) were measured using SEC on a 1100HP Chemstation equipped with a 300–7.5 mm PLgel Mixed-D 5 mm/104 A° column. Detection was performed by a diode array UV-vis detector and a refractive index detector. The column temperature and the flow rate were fixed to 313 K and 1 $mLmin^{-1}$, respectively. The calibration curve was built using 10 polystyrene (PS) narrow standards (S-M-10* kit from Polymer Labs) and all molecular weights are therefore given in equivalents of PS (eq. PS). Two runs of 20 mL injection of ca. 2 mg/ml polymer in HPLC grade THF solutions were typically analyzed for each sample with UV-vis detection located at 355 nm. Electrochemical polymerizations of the synthesized macromonomers were carried out in a one compartment, three-electrode electrochemical cell equipped with a flat platinum working electrode (7 mm^2), a Pt wire counter electrode, and an Ag/Ag silver wire reference electrode. The electrolyte consisted of 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP) solution in dichloromethane containing 2 x 10^{-3} M macromonomer. For the characterisation of photovoltaic properties, bulk heterojunction solar cells were fabricated using a classical device design on a glass substrate covered by a transparent conductive oxide, ITO (indium-tin-oxide), according to the procedure and layout described in ref. 17. The ITO layer was covered with an 80 nm thick interfacial PEDOT/PSS layer (Baytron-P1). The active layer was spin-coated onto the PEDOT layer from chlorobenzene solutions containing the mixture of donor and PCBM. Finally, a 1.3 nm thick layer of LiF was evaporated on top of the active layer and covered by the aluminium electrode (100 nm). The active surface of the device was 28 mm^2. Current–voltage characteristics and power conversion efficiencies of the solar cells were measured in inert atmosphere via a computer controlled Keithley1 SMU 2400 unit using 1000 W m^{-2} air-mass (1.5) simulated white light generated by a Oriel Solar AAA (Xe Lamp) simulator. It has to be noted that these are simulated conditions, which are however consistent with most published work to date. A monocrystalline silicon solar cell, calibrated at the Fraunhofer Institut Solare

Energiesysteme (Freiburg, Germany), was used as a reference cell to confirm stabilisation of the 1000 W m^{-2} illumination. In addition, the used apparatus was a standard class AAA system which is widely used and gives mismatch factors around 4 % in the 300 to 1100 nm range, as described by Risø Laboratory. The cell was illuminated through the ITO. The temperature of the polymer heterojunction, measured using a thermocouple (Pt100) mounted on the ITO substrate, reached 30 °C at the initial I (V) characterisation.

For the mobility measurements using the photoCELIV method, we used a laser beam operating at 532nm with 1ns light pulses. The solar cells were lit from the ITO side. After a 0.5µs delay time, the photogenerated charges are extracted by applying a ramp voltage on the device using an Agilent 33220A (the Al cathode is connected to the positive terminal). The signal was recorded on a Tektronix DPO7104 oscilloscope. The mobility value were obtained as explained in ref [3].

Synthesis

Preparation of monomer

5,5-dimethyl-2-(4-octylthiophen-2-yl)-1,3,2-dioxaborinane (1), 2,7-Bis(4-octyl-5,29-bithien-2-yl)-fluoren-9-one (5) were prepared as reported[1].

4,7-bis(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (2): A mixture of 4,7-dibromobenzo[c][1,2,5]thiadiazole (478 mg, 1.6 mmol), 5,5-dimethyl-2-(4-octylthiophen-2-yl)-1,3,2-dioxaborinane (1) (1.5 g, 4.8 mmol), and $Pd(PPh_3)_4$ (55.5 mg, 3% molar) in 2.0 M K_2CO_3 aqueous solution (5 ml) and THF (20 ml) was refluxed overnight. The mixture was then allowed to cool to room temperature before addition of 1M HCl and extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by silica gel column chromatography with hexane/chloroform (4:1 v/v) as eluent to afford 4,7-bis(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (**1**) as a brown viscous oil. (233 mg, yield: 28%)**.** ^{1}H NMR (200 MHz, $CDCl_3$, δ): 8.08 (s, 1H; Ar H), 8.07 (s, 1H; Ar H), 7.93 (s, 2H; Ar H), 7.15 (s, 1H; Ar H), 2.79 (t, *J* = 7.2 Hz, 4H; CH_2), 1.88-1.73 (m, 4H; CH_2), 1.53-1.34 (m, 20H, CH_2), 0.98 (t, *J* = 6.6 Hz ,6H; CH_3)

4,7-bis(5-bromo-4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3): 4,7-bis(4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (**1**) (417 mg, 0.79 mmol) was dissolved in 10 ml of chloroform and placed in a light protected two-neck round bootom flask. N-bromosuccinimide (297 mg, 1.67 mmol) dissolved in 10 ml of chloroform was placed in a dropping funnel, and then added drop wise to the flask at room temperature. After stirring for overnight at room temperature, the resulting mixture was poured into 20 ml of water, and then extracted with dichloromethane. After solvent removal, the crude product was purified by silica gel column chromatography with hexane/chloroform (9:1 v/v) as eluent to afford 4,7-bis(5-bromo-4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (**3**) as reddish flakes. (240 mg, 44 %) ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.77 (s, 2H; Ar H), 7.75 (2H, s; Ar H), 2.64 (t, *J* = 7.2 Hz, 4H; CH_2), 1.73-1.59 (m, 4H; CH_2), 1.43-1.26 (m, 20H; CH_2), 0.88 (t, *J* = 6.5 Hz, 6H; CH_3)

4,7-bis(3-octyl-2,2'-bithiophen-5-yl)benzo[c][1,2,5]thiadiazole (4): A mixture of 4,7-bis(5-bromo-4-octylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (**2**) (217 mg, 0.32 mmol) , 5,5-dimethyl-2-(thiophen-2-yl)-1,3,2-dioxaborinane (149 g, 0.76 mmol), and $Pd(PPh_3)_4$ (15 mg, 4% molar), K_3PO_4 (155 mg, 0.76 mmol) dissolved in 30 ml of DMF was refluxed overnight. The mixture was then allowed to cool to room temperature before addition of 1M HCl and extracted with diethyl ether. The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified by silica gel column chromatography with hexane/chloroform (4:1 v/v) as eluent to afford 4,7-bis(3-octyl-2,2'-bithiophen-5-yl)benzo[c][1,2,5]thiadiazole (**3**) as reddish powder. (50 mg, 23 %)^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.99 (s, 2H; Ar H), 7.83 (s, 2H; Ar H), 7.36 (dd, J_1 = 5 Hz, J_2 = 1.2 Hz, 2H; Ar H), 7.25 (dd, J_1 = 3.6 Hz, J_2 = 1.2 Hz, 2H; Ar H), 7.13 (dd, J_1 =5.2 Hz, J_2 = 3.6 Hz, 2H; Ar H), 2.85 (t, J= 7.2 Hz, 4H; CH_2), 1.83-1.55 (m, 4H; CH_2), 1.47-1.21 (m, 20H; CH_2), 0.88 (t, 6H, J = 6.6 Hz; CH_3). ^{13}C NMR (200 MHz, $CDCl_3$, (δ): 152.49, 140.48, 136.86, 136.01, 132.31, 130.54, 127.48, 126.01, 125.54, 125.39, 31.88, 30.66, 29.62, 29.44, 29.29, 22.68, 14.14. Elemental analysis for $C_{38}H_{44}N_2S_5$ (Calc.): C, 66.23; H, 6.44; N, 4.07; S, 23.27; Found: C, 65.53 ; H, 6.64; N, 3.88; S, 22.12

4,7-bis(5'-bromo-3-octyl-2,2'-bithiophen-5-yl)benzo[c][1,2,5]thiadiazole (BTB-C8): 4,7-bis(3-octyl-2,2'-bithiophen-5-yl)benzo[c][1,2,5]thiadiazole (**3**) (267 mg, 0.39 mmol) was dissolved in 10 ml of chloroform. N-bromosuccinimide (145 mg, 0.81 mmol) dissolved in 10 ml of chloroform was then added dropwise at room temperature. After stirring for overnight at room temperature, the resulting mixture was poured into 20 ml of water, then extracted with dichloromethane. After solvent removal, the crude product was purified by silica gel column chromatography with cyclohexaneas eluent to afford 4,7-bis(5'-bromo-3-octyl-2,2'-bithiophen-5-yl)benzo[c][1,2,5]thiadiazole (**4**) as violet powder. (312 mg, 95 %) ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.95 (s, 2H; Ar H), 7.81 (s, 2H; Ar H), , 7.05 (d, J = 3.8 Hz, 2H; Ar H), 6.97 (d, J =3.8 Hz, 2H; Ar H), 2.79 (t, J= 7.8 Hz, 4H; CH_2), 1.78-1.64 (m, 4H; CH_2), 1.21 (m, 20H; CH_2), 0.89 (t, 6H, J = 6.6 Hz; CH_3) Anal.calcd for $C_{38}H_{42}Br_2N_2S_5$: C, 53.89 ; H, 5.00 ; N, 3.31 ; S, 18.93 ; found: C, 53.67 ; H, 5.08 ; N, 3.29 ; S, 18.92

2,7-bis(5'-bromo-3-octyl-2,2'-bithiophen-5-yl)-9H-fluoren-9-one (5): 500 mg of **2,7-Bis(4-octyl-5,29-bithien-2-yl)-fluoren-9-one (4)** (0.68 mmol) were dissolved in 15 ml of chloroform in a flask at room temperature. 267 mg of NBS dissolved in 15 ml of chloroform was added drop wise to the flask and leave to stir overnight at room temperature. After overnight, the mixture was washed with water then extracted by dichloromethane, and further purify by column chromatography (silica gel, hexane/dichloromethane, 7: 3). (386 mg, yield = 64%) ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.86 (s, 2H; Ar H), 7.68 (d, J=7.8 Hz , 2H; Ar H), 7.50 (d, J = 7.8 Hz, 2H; Ar H), 7.21 (s, 2H; Ar H), 7.04 (d, J = 3.8 Hz, 2H; Ar H), 6.90 (d, J =3.8 Hz, 2H; Ar H), 2.74 (t, J= 7.6 Hz, 4H; CH_2), 1.62 (t, J= 7.6 Hz 4H; CH_2), 1.28 (m, 20H; CH_2), 0.89 (t, 6H, J = 6.6 Hz; CH_3) ; Anal.calcd for $C_{45}H_{46}Br_2OS_4$: C, 60.67; H, 5.20; S, 14.40 ; found: C, 61.94; H, 5.41; S, 14.59. All other analytical data were similar to those reported in reference [2].

2,7-bis(5-bromo-4-octylthiophen-2-yl)-9H-fluoren-9-one (6): In a light protected flask, N-bromosuccinimide (0.782 g, 4.38 mmol) was dissolved in 10 ml of chloroform at room temperature. 2,7-bis(4-octylthiophen-2-yl)-9H-fluoren-9-one (1 g, 1.758 mmol) dissolved in 20 ml of chloroform was then added drop wise to the NBS solution. After complete addition, a red precipitate was obtained and the mixture was stirred for an additional period of 12 h at room temperature. The reaction was then poured into water and extracted with diethyl ether. After solvent removal, a minimum volume of chloroform was added to dissolve the product and methanol was then added to allow precipitation and cooled in the refrigerator. Bright orange powder were then filtered and dried (0.92 g, yield: 72 %). ^{1}H NMR (200 MHz, $CDCl_3$) d (ppm): 7.78 (2H,d,J=1.6 Hz), 7.58 (2H, dd, J= 7.8 and 1.8 Hz), 7.46 (2H, d, J= 7.8 Hz), 7.07 (2H,s), 2.56 (4H, t, J= 8.05 Hz), 1.65-1.56 (4H, m), 1.20-1.70 (20H, m), 0.89 (6H, m). All other analytical data were similar to those reported in reference [2].

2,7-Bis(4-octyl-5,29-bithien-2-yl)-fluoren-9-one (7): 0.9 g of 2,7-bis(5-bromo-4-octylthien-2-yl)-fluoren-9-one (2) (1.26 mmol) and 0.62 mg of 5,5-dimethyl-2-(thien-2 yl)[1,3,2]dioxoborinane (3.15 mmol, 2.5 eq.) were placed in 50 mL of anhydrous DMF and the mixture was stirred under argon for 10 min at 60°C and then 800 mg of K_3PO_4 (3.7 mmol, 3 eq.) and 73 mg of $Pd(PPh_3)_4$ (0.06 mmol) were added. The mixture was kept at reflux for 16h with constant stirring and then allowed to cool to 25 °C. The reaction was treated with hydrochloric acid (2.0 M) and the product was extracted with diethyl ether. The crude was concentrated and dissolved in a minimum of chloroform and the addition of methanol allows precipitation of pure product. We obtained deep red precipitates. (930 mg, yield= 88 %).^{1}H NMR (200 MHz, $CDCl_3$) d (ppm): 7.85 (2H, d, J = 1.3 Hz), 7.63 (2H, dd, J = 7.9 and 1.3 Hz), 7.44 (2H, d, J = 7.6 Hz), 7.32 (2H, dd, J = 5.1 and 1.3 Hz), 7.21 (2H, s), 7.15 (2H, dd, J = 3.5 and 1.3 Hz), 7.07 (2H, dd, J = 5.1 and 3.5 Hz), 2.75 (4H, t, J = 7.3 Hz), 1.65 (4H, quint, J = 7.6 Hz), 1.40–1.20 (m, 20H), 0.9–0.8 (m, 6H). ^{13}C NMR (200 MHz, $CDCl_3$) d (ppm): 193.31, 142.64, 140.66, 140.29, 135.92, 135.03, 134.96, 131.19, 130.88, 127.45, 126.58, 125.90, 125.44, 120.98, 120.74, 31.89, 30.57, 29.59, 29.43, 29.26, 22.68, 14.13. Elemental analysis for $C_{45}H_{48}OS_4$ (calculated): C, 73.72 %; H, 6.60 %; Elemental analysis (found): C, 73.42%; H, 6.50%.

2,7-bis(5'-bromo-3-octyl-2,2'-bithiophen-5-yl)-9H-fluoren-9-one (BTF-C8): 500 mg of 2,7-Bis(4-octyl-5,29-bithien-2-yl)-fluoren-9-one (0.68 mmol) (17) were dissolved in 15 ml of chloroform in a flask at room temperature. 267 mg of NBS dissolved in 15 ml of chloroform was added drop wise to the flask and leave to stir overnight at room temperature. After overnight, the mixture was washed with water then extracted by dichloromethane, and further purified by column chromatography (silica gel, hexane/dichloromethane, 7: 3). (386 mg, yield = 64%) ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.86 (s, 2H; Ar H), 7.68 (d, *J*=7.8 Hz , 2H; Ar H), 7.50 (d, *J* = 7.8 Hz, 2H; Ar H), 7.21 (s, 2H; Ar H), 7.04 (d, *J* = 3.8 Hz, 2H; Ar H), 6.90 (d, *J* =3.8 Hz, 2H; Ar H), 2.74 (t, *J*= 7.6 Hz, 4H; CH_2), 1.62 (t, J= 7.6 Hz 4H; CH_2), 1.28 (m, 20H; CH_2), 0.89 (t, 6H, *J* = 6.6 Hz; CH_3) ; Elemental analysis for $C_{45}H_{46}Br_2OS_4$ (calculated): C, 60.67; H, 5.20; S, 14.40 ; found: C, 61.94; H, 5.41; S, 14.59. All other analytical data were similar to those reported in reference [2].

3-(2-ethylhexyl)thiophene: 1.97g (81mmol) of magnesium is activated by heat under high vacuum. 30mL of distillated THF is added. Separately, 14.2g (73.6 mmol) of 2-ethylhexyl bromide is diluted in 12 mL of distillated THF and added drop by drop to Mg. After the addition, reflux is maintained during 1h. 10g (61.34 mmol) of 3-bromothiophene is diluted in 25 mL of distillated THF and 332 mg of catalyst is added to the flask. The temperature is reached to 0°C and (2-ethylhexyl)magnesium bromide is slowly added. The reaction turned black quickly. After 6 hours, HCl 1M is added and the product is extracted by Et_2O, dried over $MgSO_4$ and concentrated. The pure compound is obtained by chromatography over silica gel with hexane as eluent. 8.85g of colorless oil is obtained (74%). RMN ^{1}H ($CDCl_3$, 200MHz): δ= 7.23 (dd, 1H, J= 3.0, 4.8 Hz), 6.90 (m, 2H), 2.56 (d, 2H, J= 6.7 Hz), 1.56 (m, 1H), 1.36-1.22 (m, 8H), 0.87 (m, 6H). RMN ^{13}C ($CDCl_3$, 200MHz): δ= 141.8, 128.7, 124.7, 120.6, 40.3, 34.2, 32.4, 28.8, 25.6, 23.0, 14.1, 10.8.

(5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)trimethylsilane (8): 10g (64 mmol) of trimethyl(thiophen-2-yl)silane is diluted in 80 mL of distillated THF. Temperature is reached to -78°C and 30 mL of Butyllithium in solution in hexane (dosed at 2.3 M, 68 mmol) is added drop by drop. Temperature is kept between -78°C and -30°C during 1h and then 14.26 mL (128 mmol) of Trimethylborate is added. The reaction is warm to room temperature and stirred 1h. HCl 0.1M is added. The product is extracted by Et_2O. The organic layer is washed twice by water and once by saturated aqueous solution of NaCl. Then, 16.66 g (160 mmol) of neopentylglycol is added with $MgSO_4$. Magnetic stirrer is kept during 1h before filtration, concentration and purification by chromatography over silica with pentane/Et_2O (90/10 vol). 10.78 g of the desired compound are obtained as a white solid. Yield of 63%. RMN ^{1}H ($CDCl_3$, 200MHz): δ= 7.62 (d, *J* = 3.28 Hz, 1H), 7.30 (d, *J* = 3.27 Hz, 1H), 3.77 (s, 4H), 1.03 (s, 6H), 0.32 (s, 9H) ; RMN ^{13}C ($CDCl_3$, 200MHz): δ= 147.1, 136.4, 134.9, 72.3 (2C), 32.0, 21.8 (2C), -0.1 (3C)

2-bromo-3-(2-ethylhexyl)thiophene (9): 2 g (10.2 mmol) of 3-(2-ethylhexyl)thiophene are dissolved in 20 mL of CHCl3 and 10 mL of acetic acid. 1.906 g (10.7 mmol, 1.05 eq.) of N-bromosuccinimide is added portion wise to the solution previously cold at 0°C. After 3 hours, 40 mL of CHCl3 are added to the solution which is washed with NaOH 0.5M, twice by water, then dried over MgSO4, concentrated under vacuum. The crude product is purified by distillation in a Kugelrohr system under vacuum at 150°C (according to the vacuum efficiency). 2.47 g (Yield 88%) of desired compound are obtained. RMN ^{1}H ($CDCl_3$, 200MHz): δ=7.18 (d, *J* = 5.6 Hz, 1H), 6.76 (d, *J* = 5.6 Hz, 1H), 2.49 (d, *J* = 7.1 Hz, 2H), 1.69-1.48 (m, 1H), 1.39-1.17 (m, 8H), 0.88 (t, *J* = 7.2, 6H).

(3'-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)trimethylsilane (10): 550 mg (4 mmol) of **(5-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)thiophen-2-yl)trimethylsilane (8)**, 500 mg (3.63 mmol) of **2-bromo-3-(2-ethylhexyl)thiophene (9)** are solubilized in 20 mL of THF. Solution is degassed by 4 consecutives freeze-pump-thaw cycles. Then 33 mg (1% molar) of Pd_2dba_3, 21 mg of $(tBu)_3PHBF_4$, then 2.2 mL of 1M aqueous and degazed solution of K_2CO_3 (1.2 eq.) are added. The tube is placed in a 70°C oil bath and stirring is kept during

14 hours. Then solution is cool down to room temperature, Et_2O is added and organic phase is washed by water, NaCl saturated, dried over $MgSO_4$. Solvent is evaporated. The purification is performed by chromatography over silica gel with pentane as eluent. 507 mg (88% yield) of a viscous liquid is obtained. RMN ^1H (CD_2Cl_2, 200MHz): δ= 7.22-7.13 (m, 3H), 6.92 (d, *J* = 5.21 Hz, 1H), 2.70 (d, *J* = 7.22 Hz, 2H), 1.73-1.54 (m, 1H), 1.39-1.12 (m, 8H), 0.93-0.76 (m, 6H), 0.33 (s, 9H) ; RMN ^{13}C (CD_2Cl_2, 200MHz): δ= 141.4, 140.4, 138.6, 134.1, 131.1, 130.5, 127.3, 123.4, 40.2, 33.2, 32.5, 28.7, 25.7, 23.0, 14.1, 10.7, -0.1 ; HRMS (M+H+): calculated for $C_{19}H_{30}S_2Si$: 351.16365, found 351.1635 ; Elemental Analysis: calculated C, 65.08; H, 8.62; S, 18.29 and found C, 64.90; H, 8.54; S: 17.88

(5'-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-3'-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)trimethylsilane (11): 980 mg of **(3'-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)trimethylsilane (10)** is solubilized in 15 mL of distillated THF. Temperature is reached to -78°C and 1.25 mL of Butyllithium in solution in hexane (dosed at 2.3 M, 2.8 mmol) is added drop by drop. Temperature is kept between -78°C and -30°C during 1h and then 0.63 mL (5.6 mmol) of trimethylborate is added. The reaction is warm to room temperature and stirred 1h. HCl 0.1M is added. The product is extracted by Et_2O. The organic layer is washed twice by water and once by saturated aqueous solution of NaCl. Then, 730 mg (7 mmol) of neopentylglycol is added with $MgSO_4$. Magnetic stirrer is kept during 1h before filtration, concentration and purification by chromatography over silica with pentant/Et_2O (90/10 vol). 608 mg of the desired compound are obtained as a white solid. Yield: 51%. RMN ^1H ($CDCl_3$, 200MHz): δ= 7.34 (s, 1H), 7.21 (d, *J* = 3.43 Hz, 1H), 7.16 (d, *J* = 3.43 Hz, 1H), 3.76 (s, 4H), 2.69 (d, *J* = 7.27 Hz, 2H), 1.73-1.59 (m, 1H), 1.39-1.14 (m, 8H), 1.03 (s, 6H), 0.90-0.76 (m, 6H), 0.38-0.28 (m, 9H)

4,7-bis(3-(2-ethylhexyl)-5'-(trimethylsilyl)-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole (12): 605 mg (1.31 mmol) of **(5'-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-3'-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)trimethylsilane (11)**, 175 mg (0.59 mmol) of dibromobenzothiadiazole are solubilized in 15 mL of THF and 15 mL of toluene. The solution is degazed by 4 consecutive freeze-pump-thaw cycles and 27 mg (4 %, 0.023 mmol) of $Pd(PPh_3)_4$ is added. 1.31 mL of 1M K_2CO_3 aqueous solution is added and the tube is dept in 90°C oil bath. After 24 hours, the reaction is stopped. The solution is washed by water; the organic layers are separated and filtrated on celite. Solvent is removed and purification by chromatographic column on silica gel is performed using cyclohexane and then 2 % of $CHCl_3$ in cyclohexane as eluent. 160 mg of pure compound is obtained (32% yield). RMN ^1H ($CDCl_3$, 200MHz): δ= 7.96 (s, 2H), 7.83 (s, 2H), 7.30 (d, *J* = 3.44 Hz, 2H), 7.21 (d, *J* = 3.45 Hz, 2H), 2.81 (d, *J* = 7.18 Hz, 4H), 1.86-1.66 (m, 2H), 1.50-1.17 (m, 16H), 0.96-0.80 (m, 12H), 0.41-0.33 (m, 18H)

4,7-bis(5'-bromo-3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole (BTB-C2C6): 160 mg (1.92 mmol) of **4,7-bis(3-(2-ethylhexyl)-5'-(trimethylsilyl)-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole (12)** is solubilized in 50 mL of $CHCl_3$. 69 mg (2.02 equivalents) of NBS are added portion wise. The reaction is protected from the light and let stir 3h30. Water is added and the organic layer is extracted washed again by

H_20, dried over $MgSO_4$ and concentrated. Purification by chromatographic column on silica gel is performed using cyclohexane and then 3 % of toluene in cyclohexane as eluent. 90 mg of pur compound is obtained (45% yield).1H NMR (200 MHz, *CDCl*$_3$) δ ppm: 7.93 (s, 2H), 7.82 (s, 2H), 7.05 (d, *J* = 3.85 Hz, 2H), 6.97 (d, *J* = 3.85 Hz, 2H), 2.74 (d, *J* = 7.23 Hz, 4H), 1.84-1.63 (m, 2H), 1.39-1.15 (m, 16H), 0.88 (t, *J* = 7.22, 7.22 Hz, 6H) HRMS : (M+) : m/z calculated for $C_{38}H_{42}Br_2N_2S_5$: 844.03128, found 844.0315; Elemental Analysis: calculated C, 53.89; H, 5.00; Br, 18.87; N, 3.31; S, 18.93 and found C, 53.58; H, 4.99; S, 19.41

2,7-diiodo-9H-fluoren-9-one (14): 5 g of fluorenone (27.7 mmol) are solubilized in 100 mL of $CHCl_3$. 50 mL of AcOH and 12 mL of H_2SO_4 are added. The temperature is increased to 70°C. 13.7 g of N-iodosuccinimide (61 mmol) are added portion wise every 2 min. The flask is protected from light and refluxing and stirring are kept for 6 hours. The reaction is poured in 400 mL of cold aqueous NaOH 2M. Organic compound are extracted by $CHCl_3$. The organic layer is then washed by water, dried over $MgSO_4$ and the solvent is evaporated. The crude product is recristallised in EtOH to afford 9.3 g of a yellow solid (78% yield). RMN ^{1}H ($CDCl_3$, 200MHz): δ= 7.95 (dd, 2H, J = 1.6, 0.5 Hz, H), 7.83 (dd, 2H, *J* = 7.8, 1.6 Hz, H), 7.26 (dd, 2H, *J* = 7.8, 0.5 Hz, H). RMN ^{13}C ($CDCl_3$, 200MHz): δ= 190.9 (1C), 143.4 (2C), 142.9 (2C), 134.7 (2C), 133.5 (2C), 122.1 (2C), 94.5 (2C). Elemental Analysis: C, 36.14; H, 1.40; I, 58.75; O, 3.70

(3'-(2-ethylhexyl)-5'-(trimethylstannyl)-[2,2'-bithiophen]-5-yl)trimethylsilane (13): 0.507 g (1.45 mmol) of **(3'-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)trimethylsilane (10)** is diluted in 30 mL of freshly distilled THF. Temperature is erached to -78°C. 0.73 mL of a 2.2M solution of BuLi (1.59 mmol) in hexane is added dropwise. The temperature is kept below -40°C during 45 min and then 1.6 mL of a 1M solution of trimethyltin chloride in hexane is added dropwise. The solution is let reach room temperature during 2 hours. Et_2O is added and organic layer is washed by aqueous NH_4Cl, H_2O, and brine before drying over $MgSO_4$. The yield is estimated by NMR to 85%. 926 mg of colored oil is obtained and used without further purification.

2,7-bis(3-(2-ethylhexyl)-5'-(trimethylsilyl)-[2,2'-bithiophen]-5-yl)-9H-fluoren-9-one (15): 920 mg of 85% pure of (3'-(2-ethylhexyl)-5'-(trimethylstannyl)-[2,2'-bithiophen]-5-yl)trimethylsilane, 317 mg of diiodofluorenone are solubilized in 15 mL of toluene and 3 mL of DMF. The solution is degassed by 3 consecutive freeze-pump-thaw cycles. 51 mg of $Pd(PPh_3)_4$ is added (0.06 eq.) and the tube is put in a 75°C oil bath during 20 hours. The solution is washed by a 5% NH_4Cl solution, then water and finally dried over $MgSO_4$. Very quick chromatography purification is performed with $CHCl_3$:C_6H_{14} (1:1 vol.) as eluent. The pure product is obtained after recristallization in acetone. 406 mg of dark red solid is obtained (yield of 63%). 1H NMR (200 MHz, *CDCl*$_3$, δ ppm 7.90 (d, *J* = 1.16 Hz, 2H), 7.68 (dd, *J* = 7.81, 1.60 Hz, 2H), 7.49 (d, *J* = 7.91 Hz, 2H), 7.21 (q, *J* = 4.21, 3.84, 3.84 Hz, 6H), 2.72 (d, *J* = 6.74 Hz, 4H), 1.83-1.59 (m, 2H), 1.48-1.13 (m, 16H), 0.87 (t, *J* = 7.13, 7.13 Hz, 12H), 0.35 (s, 18H); 13C NMR (200 MHz, *CDCl*$_3$, δ ppm 193.4, 142.6, 141.0, 140.8, 140.0, 139.8, 135.1, 134.2, 131.7, 131.3, 127.4 (2C), 127.2, 121.0, 120.7, 40.2, 33.6, 32.6, 28.7, 25.7, 23.0, 14.1, 10.8, -0.1

2,7-bis(5'-bromo-3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-9H-fluoren-9-one (BTF-C2C6)

400 mg (0.46 mmol) of 2,7-bis(3-(2-ethylhexyl)-5'-(trimethylsilyl)-[2,2'-bithiophen]-5-yl)-9H-fluoren-9-one () is solubilized in 50 mL of $CHCl_3$. The temperature is cooled down to 0°C. 166 mg (0.93 mmol) of NBS is added by small portions. After 2h at 0°C and 2h at room temperature, H_2O is added and organic layer are extracted, washed by water and dried over $MgSO_4$. Purification by chromatography on silica gel is performed using cyclohexane and 5 to 8 % of toluene as eluent. 392 mg of black red powder are obtained (yield of 94 %).
1H NMR (400 MHz, *CDCl*$_3$, δ ppm 7.84 (d, *J* = 1.72 Hz, 2H), 7.63 (dd, *J* = 7.79, 1.76 Hz, 2H), 7.45 (d, *J* = 7.83 Hz, 2H), 7.16 (s, 2H), 7.02 (d, *J* = 3.83 Hz, 2H), 6.88 (d, *J* = 3.84 Hz, 2H), 2.64 (d, *J* = 7.21 Hz, 4H), 1.71-1.59 (m, 2H), 1.40-1.18 (m, 16H), 0.86 (t, *J* = 7.11, 7.11 Hz, 12H); 13C NMR (400 MHz, *CDCl*$_3$, δ ppm 193.2, 142.7, 140.8, 140.5, 137.3, 135.0, 134.8, 131.3, 130.3, 130.2, 126.9, 126.5, 121.0, 120.8, 112.1, 40.3, 33.5, 32.5, 28.7, 25.7, 23.0, 14.1, 10.7; Elemental Analysis: calculated C, 60.67; H, 5.20; Br, 17.94; O, 1.80; S, 14.40 and found C, 61.13; H, 5.39; S, 14.23

Synthesis of polymer

Poly [4-(5'-(9,9-dihexyl-7-(3'-octyl-2,2'-bithiophen-5-yl)-9H-fluoren-2-yl)-3-octyl-2,2'-bithiophen-5-yl)benzo[c][1,2,5]thiadiazole] ((PBTFB-C8): 4,7-bis(5'-bromo-3-octyl-2,2'-bithiophen-5-yl)benzo[c][1,2,5] thiadiazole (BTB-C8) (400 mg, 0.47 mmol), and **2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(5,5-dimethyl-1,3,2-dioxaborinane)** (238 mg, 0.47 mmol) were charged in a 25 ml flask under N_2. After adding toluene (6 ml) the mixture was degassed by following the addition of Na_2CO_3 solution (2 ml, 2.0 M) , and the catalysts $Pd(db)_3$ (8.6 mg, 9 10^{-3} mmol) and P(o-tolyl)$_3$ (17 mg, 5.4 x 10^{-2} mmol). The mixture was then heated at 120 °C for 72 h. For end-capping, 2-thiophene boronic ester (185 mg, 0.94 mmol) and 2-bromothiophene (154 mg, 0.94 mmol) were added and the mixture was heated for another 2 h. After cooling to room temperature, the mixture was poured into methanol. The precipitate was collected and washed with methanol vigorously then extracted by soxhlet extraction with acetone and chloroform. The chloroform fraction was concentrated and used for further use. (375 mg, 67 %) Mn : 5.64 kDa (eq PS) ; Mw: 8.61 kDa (eq PS); PDI: 1.56; ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.95 (s, 2H; Ar H), 7.81 (s, 2H; Ar H), , 7.05 (d, *J* = 3.8 Hz, 2H; Ar H), 6.97 (d, *J* =3.8 Hz, 2H; Ar H), 2.79 (t, *J*= 7.8 Hz, 4H; CH_2), 1.78-1.64 (m, 4H; CH_2), 1.21 (m, 20H; CH_2), 0.89 (t, 6H, *J* = 6.6 Hz; CH_3) ; ^{13}C NMR (200 MHz, $CDCl_3$, δ): 152.97, 152.22, 145.46, 145.33, 140.93, 137.25, 135.75, 133.38, 133.10, 131.16, 127.29, 125.80, 125.59, 120.17, 78.10, 77.46, 76.83, 55.79, 40.90, 32.39, 30.16, 29.96, 29.82, 23.17, 23.06, 14.62, 14.50 Anal. calcd for $C_{71}H_{80}N_2S_7$: C, 71.91; H, 6.80; N, 2.36; S, 18.93; found: C, 71.54; H, 7.01; N: 2.51; S, 14.34

Poly[2-(5'-(9,9-dihexyl-7-(3'-octyl-2,2'-bithiophen-5-yl)-9H-fluoren-2-yl)-3-octyl-2,2'-bithiophen-5-yl)-9H-fluoren-9-one] (PBTFF-C8): 2,7-bis(5'-bromo-3-octyl-2,2'-bithiophen-5-yl)-9H-fluoren-9-one (BTF-C8) (200 mg, 0.22 mmol), and **2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(5,5-dimethyl-1,3,2-dioxaborinane)** (113 mg, 0.22 mmol) were charged in a 25 ml flask under N_2. After adding toluene (6 ml), the mixture was degassed by following the addition of Na_2CO_3 solution (2 ml, 2.0 M) , and the catalysts $Pd(dba)_3$ (4 mg, 4,4 10^{-3}

mmol) and P(o-tolyl)$_3$ (8 mg, 2.6 x 10^{-2} mmol). The mixture was then heated at 120 °C for 72 h. For end-capping, of 2-thiophene boronic ester (94 mg, 0.44 mmol) and 2-bromothiophene (73 mg, 0.44 mmol) were added and the mixture was heated for another 2 h. After cooling to room temperature, the mixture was poured into methanol. The precipitates were collected and washed with methanol vigorously then extracted by soxhlet extraction with acetone and chloroform. The chloroform fraction was concentrated and used for further use. (92 mg, 33 %) ; Mn : 3.24 kDa (eq PS)**;** Mw : 4.96 kDa (eq PS)**;** I : 1.53 ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.83-6.86 (m, 16H), 2.80 (br, 4H), 2.01 (br, 4H), 1.68-1.07 (br, 40H), 0.89 (br, 6H), 0.76 (br,6H) ; ^{13}C NMR (200 MHz, $CDCl_3$, δ): 151.14, 150.45, 146.66, 142.42, 140.47, 137.99, 134.60, 134.55, 134.35, 130.71, 129.83, 129.15, 126.33, 126.25, 124.16, 120.61, 120.41, 120.371, 119.300, 119.240, 89.450, 77.234, 76.599, 75.964, 40.020, 31.528, 31.495, 31.085, 30.137, 29.299, 29.257, 23.332, 22.300, 22.178, 13.756; Anal.calcd for $C_{78}H_{84}OS_6$: C, 76.17; H, 6.88; O, 1.30; S, 15.64 ; found: C, C, 69.27; H, 6.37; S, 11.70

poly(4-(5'-(9,9-bis(2-ethylhexyl)-9H-fluoren-2-yl)-3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-7-(3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole) (PBTFB-C2C6): 200 mg (0.236 mmol) of **4,7-bis(5'-bromo-3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole (BTB-C2C6)** and 0.496 mL of 0.5M (0.248 mmol) solution in toluene of **9,9-Di(2-ethylhexyl)fluorene-2,7-diboronic acid bis(1,3-propanediol)ester** are solubilized in 12 mL of solvant (toluene only). The solution is degassed by 4 consecutive freeze-pump-thaw cycles before filling tube with Argon. 0.496 mL of 1M aqueous solution of K_2CO_3, 2 drop of Aliquat 336 and finally 10.9 mg of $Pd(PPh_3)_4$ are added to the solution. The tube is put in a pre-heated oil bath at 100°C during 42 hours. 34 mg of para-methoxybenzene boronic acid is added and after 1h30, 80 mg of iodoanisole. After 1h30, the solution is cooling down. Products are precipitated in methanol and polymer is purified by soxhlet extraction using acetone and finally chloroform. 174 mg of very dark red powder is obtained (67% yield). RMN ^{1}H ($CDCl_3$, 200MHz): δ= 8.01 (s, 2H), 7.86 (d, 2H), 7.74-7.61 (m, 6H), 7.35 (d, 2H, J=3.4 Hz), 7.25 (s, 2H), 2.88 (d, 4H, J=6.3 Hz), 2.13-2.04 (m, 4H), 1.88-1.80 (m, 2H), 1.47-1.25 (m, 18H), 0.97-0.55 (m, 40H).

Poly(2-(5'-(9,9-bis(2-ethylhexyl)-9H-fluoren-2-yl)-3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-7-(3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-9H-fluoren-9-one) (PBTFF-C2C6): 100 mg (0.112 mmol) of **2,7-bis(5'-bromo-3-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-9H-fluoren-9-one (BTF-C2C6)** and 0.235 mL of 0.5M (0.117 mmol) solution in toluene of **9,9-Di(2-ethylhexyl)fluorene-2,7-diboronic acid bis(1,3-propanediol)ester** are solubilized in 8 mL of solvant (toluene only or toluene/DMF). The solution is degassed by 4 consecutive freeze-pump-thaw cycles before filling tube with Argon. 0.235 mL of 1M aqueous solution of K_2CO_3, 2 drop of Aliquat 336 and finally 5.2 mg of $Pd(PPh_3)_4$ are added to the solution. The tube is put in a pre-heated oil bath at 100°C during 42 hours. 34 mg of para-methoxybenzene boronic acid is added and after 1h30, 80 mg of iodoanisole. After 1h30, the solution is cooling down. Products are precipitated in methanol and polymer is purified by soxhlet extraction using acetone and finally chloroform. 84 mg of very dark red powder is obtained (64% yield). RMN ^{1}H ($CDCl_3$, 200MHz): δ= 7.94 (s, 2H), 7.80-7.51 (m, 10H), 7.33 (d, 2H, J=3.4 Hz), 7.25 (s, 2H), 7.18 (d, 2H, J=3.4 Hz), 2.80 (d, 4H, J=6.3 Hz), 2.08-2.04 (m, 4H), 1.78-1.68 (m, 2H), 1.47-1.25 (m, 18H), 0.91-0.50 (m, 40H).

References:

[1] All other analytical data were similar to those reported in reference [S. K. Lee, S. Cho, M. Tong, J. H. Seo and A. J. Heeger, *J. Polym. Science Part A: Polym. Chem.,* **2011**, 49, 1821.

[2] F. Lincker, B. Heinrich, R. De Bettignies, P. Rannou, J. Pécaut, B. Grévin, A. Pron, B. Donnio, R. Demadrille, *J. Mater. Chem.*, 2011, **21**, 5238–5247

[3] Mozer, A. J.; Sariciftci, N. S.; Lutsen, L.; Vanderzande, D.; Österbacka, R.; Westerling, M.; Juška, G., *Appl. Phys. Lett.* 2005, 86 (11), 1-3.